

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
24 October 2002 (24.10.2002)

PCT

(10) International Publication Number  
WO 02/085072 A1

(51) International Patent Classification: H05B 3/26,  
3/74, C08G 77/50, H05B 3/14

S.; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL), VAN DER WOUDE, Rene, H.; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).

(21) International Application Number: PCT/IB02/01289

(74) Agent: VAN WERMESKERKEN, Stephanie, C.; Internationaal Octrooibureau B.V., Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).

(22) International Filing Date: 9 April 2002 (09.04.2002)

(25) Filing Language: English

(81) Designated States (national): CN, JP.

(26) Publication Language: English

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(30) Priority Data: 01201401.5 17 April 2001 (17.04.2001) EP

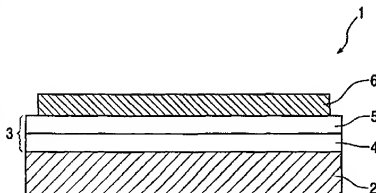
(71) Applicant: KONINKLIJKE PHILIPS ELECTRONICS N.V. [NL/NL]; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL).

Published:  
— with international search report

(72) Inventors: WIELSTRA, Ytsen; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). WINKEL, Jolanda, H.,

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: INSULATING LAYER FOR A HEATING ELEMENT



(57) Abstract: Disclosed is a heating element, at least comprising a substrate, an electrically insulating layer, and a resistive layer. The electrically insulating layer of said element comprises a layer which is obtained by means of a sol-gel process. Also described is an electrical domestic appliance comprising at least such a heating element, as well as a method of manufacturing said heating element.

WO 02/085072 A1

### Insulating layer for a heating element

The present invention relates to a heating element, at least comprising a substrate, an electrically insulating layer, and a resistive layer. Moreover, the present invention relates to an electrical domestic appliance including such a heating element, as well as to a method of manufacturing said heating element.

5 A heating element as mentioned in the preamble is for example known from US-A-5,822,675. Said patent discloses a heating element which comprises a substrate having on its surface a first layer of a silicon based electrically insulating material. Preferably said layer is also thermally conductive to transfer a high amount of heat from the electrically resistive layer. To achieve both electrical insulation and thermal conductivity, the first layer  
10 preferably includes a filler, such as for example alumina, silicon carbide, or zirconium diboride, in addition to the silicone resin. On a surface of the first layer is a second layer comprising a silicon based electrically resistive material. Attached to the second layer are at least two separate areas of silicon based electrically conductive material. Each of these separate areas are suitable for connection to a power supply.

15 A disadvantage of the above heating element is that silicon used in the electrically insulating layer is leak as it takes up water, and therefore exceeds the maximum allowable leakage current of 0.75mA as specified in IEC 335-1.

It is an aim of the present invention to provide for a heating element according to the preamble which has a relatively high breakdown voltage. In particular, the present  
20 invention aims to provide for a heating element, the substrate of which comprises aluminum or anodized aluminum. It will be clear that the term aluminum comprises both aluminum and alloys of aluminum. Furthermore, the present invention aims to provide for an electrical domestic appliance including such a heating element, as well as to a method of manufacturing said heating element.

25 These and other objects of the invention are achieved by a heating element according to the preamble which is characterized in that the electrically insulating layer comprises a layer which is obtained by means of a sol-gel process.

By applying an electrically insulating layer comprising a so-called sol-gel layer several advantages are achieved. First of all, the sol-gel layer shows excellent

electrically insulating properties. The carbon content of sol-gel materials is sufficiently low to prevent the formation of a carbonized conductive track in case of failure of the heating, thereby providing a safe heating element. Also, sol-gel materials have a high thermal conductivity which is in the order of magnitude of 0.5-2 W/m<sup>2</sup>K. Furthermore, sol-gel material can be processed at temperatures below 400°C, which makes this material suitable to be applied directly to aluminum substrates.

Although the sol-gel electrically insulating layer is especially suitable for application on aluminum substrates, other substrates which are conventionally used for heating elements and which are compatible with the final utility may also be used. Said substrates may include, for example, stainless steel, enameled steel or copper. The substrate may be in the form of a flat plate, a tube or any other configuration which is compatible with the final utility.

In particular the sol-gel process at least comprises the step of mixing an organosilane compound with water.

Said organosilane compound advantageously contains at least two hydrolytically condensable substituents.

Preferably, the sol-gel process comprises the step of mixing an organosilane compound and silica particles, in particular colloidal silica particles.

Although several organosilanes can be used, for high temperature applications heat resistant silanes are preferred. Preferred examples of such silanes are methyltrimethoxysilane (MTMS) and tetraethoxysilane (TEOS). An increase of the layer thickness of such layers can be obtained by the addition of fillers, such as colloidal silica.

In some cases it is necessary to have a certain minimum thickness of the electrically insulating layer, for example in view of the capacitive functioning of the layer. In order to obtain such thickness, the electrically insulating layer may also comprise a resin.

This can be advantageous, in particular when the sol-gel material cannot be applied in the desired thickness.

In order to obtain a screen printable electrically insulating layer, said layer advantageously comprises a resin with an insulating filler.

Said insulating fillers may comprise titanium oxide, silicon oxide, aluminum oxide, mica or iron oxide.

Preferably, the resin comprises polyimide.

Advantageously said polyimide may be filled with an insulating filler.

Polyimide is a material with a high temperature resistance and with good electrically insulating properties. The material shows no leakage up till 350°C. The insulating filler material may comprise any insulating filler as mentioned above.

However, in case of extreme load or at the end of life, the heating element may fail. In the process of failure the polyimide insulating layer may carbonize, thereby forming an electrically conducting track. It will be clear that this can result in dangerous situations.

In order to avoid such dangerous situation, the electrically insulating layer of the heating element preferably comprises at least a first layer which is obtained by means of a sol-gel process, as well as a second layer which comprises a thermoplastic resin, preferably polyimide.

In case of a breakdown voltage of the polyimide layer, the sol-gel layer will remain insulating and will act as a security of the heating element.

The present invention further relates to an electrical domestic appliance comprising at least a heating element in accordance with the present invention.

The heating elements according to the present invention are especially suitable for use in applications where high temperatures are used. These applications comprise, for example, (steam) irons, kettles, coffee makers, deep frying pans, grills, space heaters, waffle irons, toasters, ovens, water flow heaters, and the like.

Finally, the present invention relates to a method of manufacturing a heating element, at least comprising the steps of:

- providing a substrate;
- applying an electrically insulating layer on said substrate; and
- applying a resistive layer on top of the electrically insulating layer.

Said method is characterized in that the electrically insulating layer comprises a layer which is obtained by means of a sol-gel process.

The invention will be further elucidated with reference to the following embodiment, the following manufacturing example and the enclosed drawing, in which: Figure 1 shows a sectional view of an embodiment of the heating element according to the present invention.

It is noted that the various elements are purely schematic and are not drawn to scale.

The heating element 1 as shown in figure 1 is built up of a substrate 2, an insulating layer 3, and a resistive layer 6.

In the embodiment shown, the substrate 2 comprises an aluminum alloy which is used for a sole plate of an iron. Said substrate 2 is covered with a layer 3 of an electrically insulating material. In the present case, the electrically insulating layer 3 consists of a first layer 4 which is obtained by means of a sol-gel process, as well as a second layer 5 which comprises a thermoplastic resin. In this case, the thermoplastic resin comprises polyimide.

Sol gel materials can be cured at temperatures below 400°C, which makes it possible to apply said materials directly on an aluminum substrate. As the sol-gel layer 4 has a low carbon content, the creation of a conductive track is prevented, even in case of failure of the heating element. Thus, the insulating properties of the sol-gel layer 4 remain intact, even in extreme situations. Moreover, the thermal conductivity of sol-gel materials is quite high and is in the order of magnitude of 0.5-2 W/m°K.

As a result of certain requirements on heating elements the thickness of the electrically insulating layer has to be about 30-60 µm. As it is difficult to build up such a thick layer by means of sol-gel techniques, a polyimide layer 5 is applied on top of the sol-gel layer in order to provide for the desired thickness. However, the sol-gel layer is as thick as possible in order to make use of all its advantages as disclosed in the above.

Example:

Method of manufacturing a heating element according to the present invention

The method of manufacturing the heating element according to the present invention at least comprises the following steps:

- providing a substrate;
- applying an electrically insulating layer on said substrate; and
- applying a resistive layer on top of the electrically insulating layer.

Below the different steps in the manufacturing method will be further elucidated.

*Substrate:*

The first step in the manufacturing method is to provide a substrate. In the present case, referring to the above embodiment and the drawing, the substrate comprises an anodized aluminum plate which can be used as a sole plate for an iron. In order to ensure

proper adhesion between all the layers the aluminium substrate has to be cleaned thoroughly. In the present case, the substrates is cleaned according to the following procedure:

- the substrate is subjected to "Ultrasonic" cleaning (ca 1 min) in a 5% solution of neutral soap in de-mineralized water (Unitech Ultrasonic Cleaner);
- 5 - then the substrate is washed out, subsequently, in a water bath, in streaming tap water, and with demi water;
- finally the substrate is dried at 80°C.

*Application of an electrically insulating layer on the substrate;*

10 *Preparation of sol-gel insulating material*

The sol-gel coatings used in the present exemplary embodiments were based on a mixture of methyltrimethoxysilane (MTMS), Ludox AS40 (40 weight % colloidal silica suspension in water), ethanol and maleic acid. SiO<sub>2</sub> sol was prepared by a single-step acid catalyzed synthetic method. Methyltrimethoxysilane (MTMS) (Aldrich Co., USA), ethanol  
15 (Merck), maleic acid and H<sub>2</sub>O (from Ludox) were combined in the molar ratio 1: 1.37: 0.0166: 4.5. MTMS, EtOH and maleic acid were mixed at room temperature for a 2 min. Ludox AS40 (DuPont) was added and solution was mixed for 60 min. After mixing solution of sol was filtered through 5 and 2 µm filters. The weight ratio of Ludox and MTMS was 0.99. The recipe used and preparation procedure for applied sol- gel system are given below.

20

Sol-gel recipe:

- |        |   |
|--------|---|
| Step 1 | MTMS (40 g) + ethanol (18.5 g) + maleic acid (0.568 g)  |
|        | Stirring during 1-2 min (maleic acid must be dissolved) |
| Step 2 | Addition of Ludox (AS-40) (39.6 g)                      |
| 25     | Stirring during 60 min.                                 |

After preparation, the silica sol solutions were filtered through 5 and 2 µm pore size filters (Whatman, New Jersey, USA) just before use to remove particles, which potentially may be present.

30

*Application of a first sol-gel layer on the substrate*

The sol-gel layer was applied on the aluminum surface within 2 hours after cleaning of the aluminum substrate.

The sol-gel layer was applied on the aluminum substrate by means of spin coating. Alternatively the sol gel layer may be applied by spray coating. The procedure used in the present example was spin coating during 5 s at 400 (low) rpm followed by spin coating during 10 s at 800 (high) rpm, yielding a final thickness of the sol-gel layer of about 3-4  $\mu\text{m}$  in one run. The coated substrate was thermally treated (dried) at 100°C for 10 min to remove the solvent. This was done on a hotplate inside a clean room. After the drying stage, the substrate coated with sol-gel material is cured at 375°C in a muffle furnace under air atmosphere during 20 min.

#### 10 *Application of further sol-gel layers*

The resulting sol-gel layer is hydrophobic preventing proper adhesion of subsequent sol-gel layers and/or the polyimide layer. Pretreatment of the resulting layer by "flame" or UV/ozone to render the surface hydrophilic is therefore necessary. The required final layer thickness of the sol-gel insulating material therefore can be obtained by multiple cycles of spin coating - curing - flame treatment. Proper adhesion of the PI layer not only requires flame treatment of the sol gel layer but also the use of an adhesion promotor like 3-aminopropyltrimethoxysilane (APS) which is applied from a diluted solution in deionized water

#### 20 *Application of an PI-insulating layer*

The polyimide layer is prepared via a condensation reaction of polyamic acid (PAA) solution in NMP. The material used in this example is RC-5019 of Pyre-M.L. The high viscosity of this solution makes it possible to spincoat relatively thick layers of this material. A dried layer thickness of up to 20  $\mu\text{m}$  is possible by a spin coating treatment of 5 s at 400 (low) rpm followed by spin coating during 10 s at 800 (high) rpm

After spin coating the layer is dried at 150°C for 10 minutes. After cooling down a second layer can be applied in the same way without further treatment. The elements are then finally cured at 375°C for 30 minutes.

#### 30 *Application of the resistive layer on top of the electrically insulating layer*

The resistive or heat generating layer is applied using the screen printing technique. In the present case the resistive layer comprises a heat-generating track. The heat-generating track is a mixture of carbon and PAA (Pyre-M.L. RC-5019). This mixture behaves

as a paste, as required for the screen printing process. The layer need to be dried at 80°C for 10 minutes to flash off the NMP.

5 Other layers like the contacting tracks made of silver filled PAA and topcoat materials can be printed in the same way as the resistive layer using screen printing with subsequent drying.

Finally the whole stack needs to be cured at 375°C for 30 minutes in order to imidize the PAA to PI.



## CLAIMS:

1. A heating element, at least comprising a substrate, an electrically insulating layer, and a resistive layer, characterized in that the electrically insulating layer comprises a layer which is obtained by means of a sol-gel process.

2. A heating element as claimed in claim 1, characterized in that the sol-gel process at least comprises the step of mixing together an organosilane compound and water.

3. A heating element as claimed in claim 1, characterized in that the sol-gel process at least comprises the step of mixing together an organosilane compound and silica particles.

4. A heating element as claimed in claim 2 or 3, characterized in that the organosilane compound comprises methyltrimethoxysilane (MTMS) or tetraethoxysilane (TEOS).

5. A heating element as claimed in claim 1, characterized in that the electrically insulating layer also comprises a resin.

6. A heating element as claimed in claim 5, characterized in that the resin comprises polyimide.

7. A heating element as claimed in claim 6, characterized in that the polyimide is filled with an insulating filler.

8. A heating element as claimed in claim 1, characterized in that the electrically insulating layer comprises at least a first layer which is obtained by means of a sol-gel process, as well as a second layer which comprises a thermoplastic resin.

9. A heating element as claimed in claim 6, characterized in that the second layer comprises a polyimide layer.
10. An electrical domestic appliance comprising at least a heating element in  
5 accordance with any one of claims 1 to 9.
11. A method of manufacturing a heating element according to any one of claims 1 to 9 at least comprising the steps of:
- providing a substrate;
  - 10 - applying an electrically insulating layer on said substrate; and
  - applying a resistive layer on top of the electrically insulating layer,
- characterized in that the electrically insulating layer comprises a layer which is obtained by means of a sol-gel process.

1/1

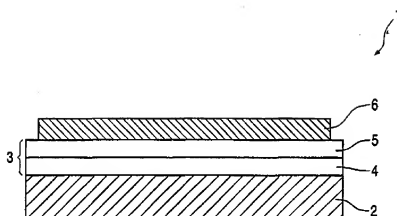


FIG. 1

## INTERNATIONAL SEARCH REPORT

Intern. Application No.

PC1/10 02/01289

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H05B3/26 H05B3/74 C06G77/50 H05B3/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H05B C06G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 954 201 A (WHITE CONSOLIDATED IND INC) 3 November 1999 (1999-11-03)	1,10,11
Y	abstract column 2, line 46-53 column 3, line 28-30 figure 1	2-4
Y	WO 98 22548 A (PHILIPS ELECTRONICS NV ;PHILIPS NORDEN AB (SE)) 28 May 1998 (1998-05-28) abstract page 1, line 1-5 page 6, line 22-34 claim 11	2-4

-/-

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"C" earlier document but published on or after the international filing date

"I" document which may throw doubts on priority claims or which is cited to establish the publication date of another claim or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

5 June 2002

Date of mailing of the international search report

11/07/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5816 Patentstr. 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl  
Fax: (+31-70) 340-3016

Authorized officer

D/L TASSA LAFOR., J

## INTERNATIONAL SEARCH REPORT

Intern      Application No  
PC1/4U    02/01289

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 790 754 A (DOW CORNING SA) 20 August 1997 (1997-08-20) page 2, line 4-11 page 3, line 25-33 page 4, line 28-30 _____	5-8

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

Intern	Application No
PCT/IB 02/01289	

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0954201	A	03-11-1999	US 5973298 A EP 0954201 A2	26-10-1999 03-11-1999
WO 9822548	A	28-05-1998	AT 210707 T CN 1214068 A DE 69709086 D1 EP 1152045 A2 EP 0896609 A1 WO 9822548 A1 JP 2000505143 T US 2001041766 A1 US 6331206 B1	15-12-2001 14-04-1999 24-01-2002 07-11-2001 17-02-1999 28-05-1998 25-04-2000 15-11-2001 18-12-2001
EP 0790754	A	20-08-1997	US 5822675 A DE 69701005 D1 DE 69701005 T2 EP 0790754 A2 JP 9232102 A	13-10-1998 03-02-2000 20-07-2000 20-08-1997 05-09-1997